INTERNATIONAL JOURNAL OF NEW HORIZONS IN THE SCIENCES (JIHSCI), Volume: 2, Issue: 1

TITANIUM DIOXIDE EFFECTS ON PERFORMANCE CHARACTERISTICS OF DIFFERENT BASED INDUSTRIAL LUBRICANTS

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ABSTRACT: *TiO2 has a wide range of usage area. Because of it's tribological properties it is also using in lubrication industry, and it has a good potential to use in different forms in different industries. Bearing control is one of the most important performance characteristics of gear oils. Besides that, additive type and amount, base oil type, ISO VG viscosity class are also important characteristics too.*

In this study, we particularly focused on bearing control and base oil types of gear oil formulations. Four different formulation type has been studied: food grade gear oil, synthetic gear oil, traditional gear oil and ester-based gear oil. All formulations are applied respectively 0.2 %-0.5 %-1 % TiO2 nanoparticles and TiO2 microparticles. We have been reported stability, FTIR spectrum, viscosity, viscosity index, weld load performance and wear scar diameters of different lubricant formulations. We have been investigated and also reported particle size effect of titanium dioxide on wear performances of different types of lubricants.

KEYWORDS: *Gear Oil, Nanoparticles, Titanium Dioxide, Tribology, Lubricant, Base Oil*

Date of Submission: 12.05.2024 Date of acceptance: 24.07.2024
https://doi.org/10.5281/zenodo.13133854

1. INTRODUCTION

Gear oil additives use to decrease friction and wear on the gear surfaces. They form a tribo-film between the working surfaces and surface temperature and contact pressure decrease according to the performance of these tribo-films.[1]

Performance of a tribo-film defines according to induction time, stability, shear stability and hardness. Performance of a tribo-film defines the performance of the gear oil.[1]

1.1 Titanium Dioxide and NP (Nanoparticle) TiO_2

Solid lubricants have been used decades to decrease the friction on the contact surface. TiO_2 is one of the most known solid lubricants. Solid lubricants are preferred for their ability of protecting sliding surfaces forming thin lubricating film and increasing the service life of the equipment.[5] And they also used in more harsh environments that liquid lubricants cannot be used.[8]

Some studies mentioned that[8,9,10] solid lubricants are effective to reducing friction for sliding contact during very long periods.

Titanium, Molybdenum and Tungsten are transition metals and all of them has a solid lubricant form respectively TiO_2, MoS_2 and WS_2.[8]

TiO_2 has a wide range of usage area. Because of it's tribological properties it is also using in lubrication industry and it has a good potential to use in different forms in different industries.[5]

There are several studies worked on TiO_2 both micro and nano form. Particle size of TiO_2 effects on the wear performance[5,8] and it has been proved that micro sized TiO_2 has an abrasive effect on surfaces.[5,6] Some studies mentioned that excessive humidity is one of the reason of that abrasion.[8,9,10,11] Despite that there are several studies reported that NP formed TiO_2 enhance the tribological properties of different types of lubricants.[8]

TiO_2 can be found and produced as anatase and rutile phases.[5] Different forms of TiO_2 has different tribological performance characteristics.[8] Waqas, M. et al. reported that TiO_2, CuO and MoS_2 showed better tribological performances in lubricants according to other NPs.

Because of their small sizes NP additives are better penetrating the contact area and as a result a more efficient lubrication could be occur.[16]

Nanoparticles cannot form stable dispersions in non-polar solvents like lubricants because of their oleophilic surface structure.[17] Nano formed additives have a potential to decrease friction but stability could be a problem for nano additives.[5]

1.2 Gear Oils

Bearing control is one of the most important performance characteristics of gear oils. Besides that, additive type and amount, base oil type, ISO VG viscosity class, foam control, water separability, corrosion control, particle size are also important characteristics too.[3]
In this study we particularly focused on bearing control and base oil types of gear oil formulations.

Mineral oil-based lubricants, ester based lubricants, greases and very different types of lubricants can be used to lubricate the gear systems.[14] For an efficient lubrication, starvation is one of the critical parameters to be focused.[14]

Liu, Heli et al.[14] mentioned in their review that improved viscosity value provided better AW performance and energy efficiency.

1.3 Food Grade Gear Oils

Legal regulations especially REACH in Europe and KKDİK in Turkey concerns the production and usage of chemicals and aim to follow the support chain from the start to the end point. Lately increasing legal concerns and some restrictions push the producers to develop more ecofriendly products.[2]
Food grade gear oils are ecofriendly and health friendly products.

Nano formed additives are more ecofriendly than traditional phosphorous based additives. That's why there is an increasing trend to investigation and using of these kinds of additives.[5]

2. MATERIAL AND METHOD

2.1 Materials and Methods

In this study TiO_2 and nanoparticular form TiO_2 (NP TiO_2) are used in commercial forms. TiO_2 is 5 µm and NP TiO2 is 20 nm-30 nm size. All the test methods applied at Petrol Ofisi Technology Centre (POTEM) by authorized personnel.

2.2 Visuals of Used Devices

Visuals of used devices are shown in figure-1. Wear scar tests applied according to ASTM D4172 test method by Stanhope-Seta Four Ball Device. Wear scar measurements are performed with Mitutoyo branded microscope which shown in figure-1. Weld load tests applied according to ASTM D2783 test method by Stanhope-Seta Four Ball Device. Stability measurements are applied according to in-house stability test method at room temperature and 50ºC with Memmert branded oven which also shown in figure-1.

Figure-1: *Visuals of Used Devices*

2.3 Formulation Design

In this study we aimed to measure some performance characteristics of NP TiO_2 and microparticle (MP) TiO_2, to compare test results and show the differences between these two different sized TiO_2 used formulation at different base oil used gear oil formulations. To show the differences we studied 4 different base oil formed gear oil formulations which are:

1. Food grade gear oil (FG GO)- we used food grade white oil
2. Synthetic gear oil (Synthetic GO)- we used poly alpha olefin base oil
3. Traditional gear oil (Traditional GO)- we used mineral base oil
4. Ester based gear oil (EB GO)- we used ester base oil

All gear oil formulation are designed at our laboratory and all formulations are applied respectively 0.2 %-0.5 %-1 % NP TiO_2 and MP TiO_2. Formulations 3 and 4 includes one more ratio than the other formulations 0.1 % NP and MP TiO_2 because even 0.2 % of these formulation series have been shown good results. Formulations 2,3 and 4 includes traditional gear oil AW and EP additive packages which are includes phosphorous despite that formulation 1 does not include traditional gear oil AW and EP additive packages because it should be an ecofriendly and health friendly formulation.

Table-1: *Food Grade Gear Oil (FG GO) (Formulation series-1)*

FORMULATION OF GEAR OIL, % WEIGHT	1	2	3	4	5	6	7
GEAR OIL WITH FOOD GRADE BASE OIL	100	99,8	99,5	99	99,8	99,5	99
TI02 (20-30nm)		0,2	0,5	1			
TI02 (5 µm)					0,2	0,5	1

Table-2: *Synthetic Gear Oil (Synthetic GO) (Formulation series-2)*

FORMULATION OF GEAR OIL, % WEIGHT	1	2	3	4	5	6	7
GEAR OIL WITH SYNTHETIC BASE OIL	100	99,8	99,5	99	99,8	99,5	99
TI02 (20-30nm)		0,2	0,5	1			
TI02 (5 µm)					0,2	0,5	1

Table-3: *Traditional Gear Oil (Traditional GO) (Formulation series-3)*

FORMULATION OF GEAR OIL, % WEIGHT	1	2	3	4	5	6	7	8	9
GEAR OIL WITH TRADITIONAL BASE OIL	100	99,9	99,8	99,5	99	99,8	99,5	99	98,8
TI02 (20-30nm)		0,1	0,2	0,5	1				
TI02 (5 µm)						0,2	0,5	1	1,2

Table-4: *Ester Based Gear Oil (EB GO) (Formulation series-4)*

FORMULATION OF GEAR OIL, % WEIGHT	1	2	3	4	5	6	7	8	9
GEAR OIL WITH ESTER BASED BASE OIL	100	99,9	99,8	99,5	99	99,8	99,5	99	98,8
TI02 (20-30nm)		0,1	0,2	0,5	1				
TI02 (5 µm)						0,2	0,5	1	1,2

Ester based oils need generally less additive to perform the same performance characteristics according to mineral base oils.[2] This good performance could be attributed to their good lubricity. Because of their polar groups they can make good attractions with metallic surfaces which are also polar too.[2]

3. RESULTS AND DISCUSSION

3.1 General Properties of GO Formulations

As shown in table-5 viscosity characteristics of GO formulations are ISO VG 68 grade which has been aimed to see the wear characteristics clearer and eliminate the differences which are coming from viscosity differences.

Table-5: *General properties of GO formulations*

General Properties of Gear Oil Formulations	Unit	Test Method	FG GO	Synthetic GO	Traditional GO	EB GO
Vis. Kin., 40°C	cSt	D445	68,92	70,8	64,9	67,3
Vis. Kin., 100°C	cSt	D445	9,05	11,7	8,4	11,9
Viscosity Index		D2270	106	161	98	178
4 Ball Weld Load	kg	D2783	80	250	200	100
4 Ball Wear Scar	mm	D4172	0,73	0,34	0,40	0,71

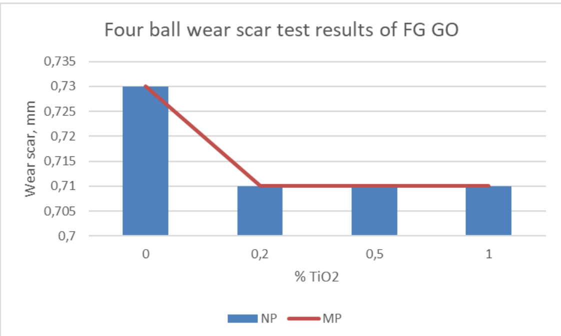
Higher viscosities mean that metal-metal contact is less at the same temperature. To eliminate the viscosity difference effect on sliding surfaces we used same viscosity grade for different base oil types.

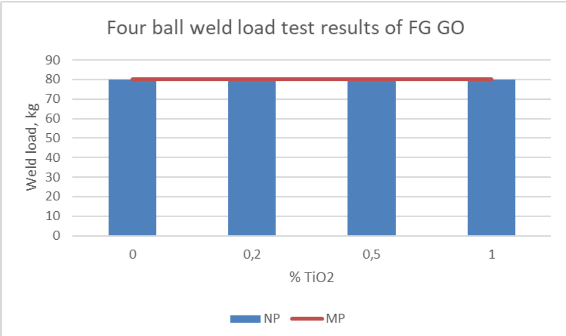
3.2 Four Ball Wear Scar and Weld Load Results of GOs

As seen in table-6 particle size differences of NPs and MPs has not a significant effect on food grade gear oil formulations.

Table-6: *Food Grade Gear Oil (FG GO)*

FORMULATION OF GEAR OIL, % WEIGHT	1	2	3	4	5	6	7
GEAR OIL WITH FOOD GRADE BASE OIL	100	99,8	99,5	99	99,8	99,5	99
TI02 (20-30nm)		0,2	0,5	1			
TI02 (5 µm)					0,2	0,5	1
4 Ball Weld Load, kg	80	80	80	80	80	80	80
4 Ball Wear Scar, mm	0,73	0,71	0,71	0,71	0,71	0,71	0,71



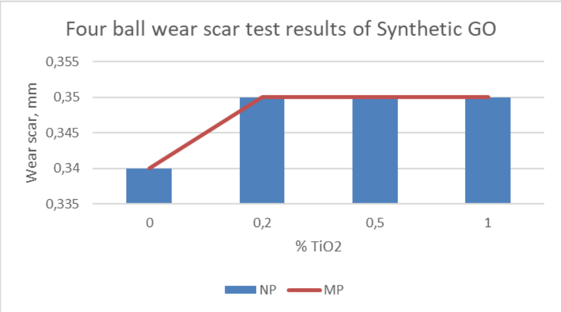


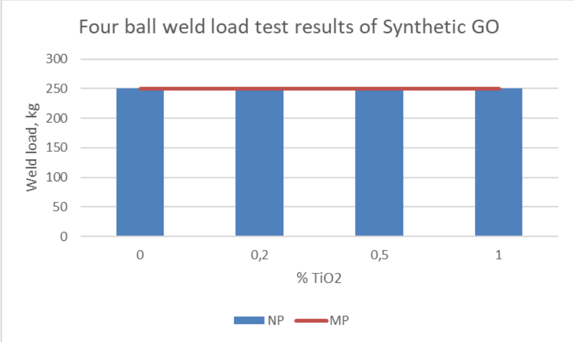
Despite the size effect was not significant, both NP and MP formulations showed better wear scar performances with TiO_2 from 0,2 % to 1 % ratios in FG GO formulations.

As seen in table-7 particle size differences of NPs and MPs has not a significant effect on synthetic gear oil formulations.

Table-7: *Synthetic Gear Oil (Synthetic GO)*

FORMULATION OF GEAR OIL, % WEIGHT	1	2	3	4	5	6	7
GEAR OIL WITH SYNTHETIC BASE OIL	100	99,8	99,5	99	99,8	99,5	99
TI02 (20-30nm)		0,2	0,5	1			
TI02 (5 µm)					0,2	0,5	1
4 Ball Weld Load, kg	250	250	250	250	250	250	250
4 Ball Wear Scar, mm	0,34	0,35	0,35	0,35	0,35	0,35	0,35



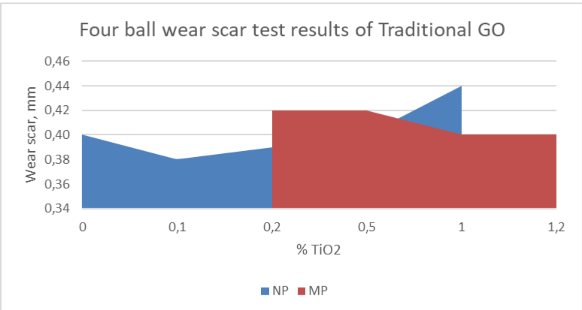


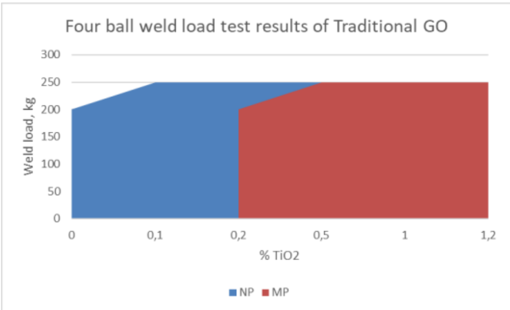
Despite the size effect was not significant, both NP and MP formulations showed worse wear scar performances with TiO_2 from 0,2 % to 1 % ratios in synthetic GO formulations.

On the contrary, as seen in table-8 particle size differences of TiO_2 NPs and TiO_2 MPs have significant and different performance effect on traditional gear oil formulations. Different particle sizes resulted different tribological performance phenomena. Increasing TiO_2 NP concentration resulted with increasing wear scar diameters. The best wear scar characteristics reported at the least concentration of TiO_2 NPs. On the other hand, increasing TiO_2 MP concentration resulted with increasing wear scar test results until 1 % ratio, after this level increasing TiO_2 MP concentration resulted with decreasing wear scar test results for traditional GO formulations.

Table-8: *Traditional Gear Oil (Traditional GO)*

FORMULATION OF GEAR OIL, % WEIGHT	1	2	3	4	5	6	7	8	9
GEAR OIL WITH TRADITIONAL BASE OIL	100	99,9	99,8	99,5	99	99,8	99,5	99	98,8
TI02 (20-30nm)		0,1	0,2	0,5	1				
TI02 (5 µm)						0,2	0,5	1	1,2
4 Ball Weld Load, kg	200	250	250	250	250	200	250	250	250
4 Ball Wear Scar, mm	0,40	0,38	0,39	0,40	0,44	0,42	0,42	0,40	0,40



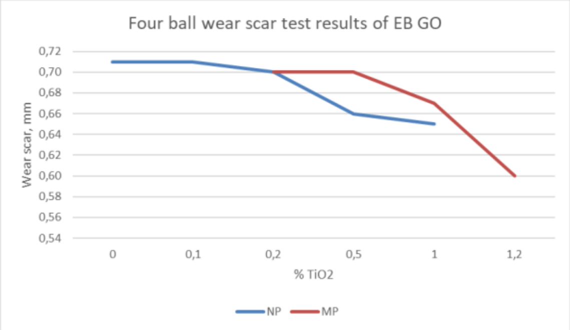


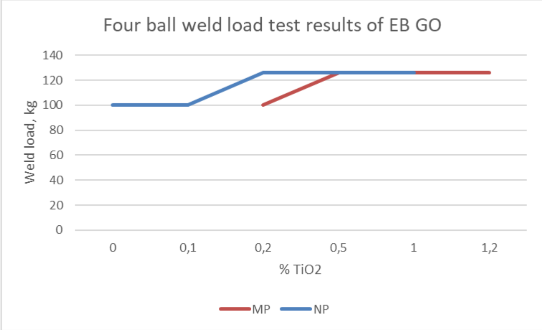
Despite the different wear scar test results and phenomena weld load performance characteristics of TiO_2 NPs and TiO_2 MPs are similar tendencies. Increasing TiO_2 NPs and TiO_2 MPs ratios resulted with increasing weld load capabilities for both additive types. Additionally, TiO_2 NPs have better performance characteristics with smaller ratios.

As seen in table-9 particle size differences of NPs TiO_2 and MPs TiO_2 have a significant effect on EB GO formulations. According to test results wear scar characteristics of TiO_2 NPs have better performance results at same ratios as compared to TiO_2 MPs in EB GO formulations.

Table-9: *Ester Based Gear Oil (EB GO)*

FORMULATION OF GEAR OIL, % WEIGHT	1	2	3	4	5	6	7	8	9
GEAR OIL WITH ESTER BASED BASE OIL	100	99,9	99,8	99,5	99	99,8	99,5	99	98,8
TI02 (20-30nm)		0,1	0,2	0,5	1				
TI02 (5 µm)						0,2	0,5	1	1,2
4 Ball Weld Load, kg	100	100	126	126	126	100	126	126	126
4 Ball Wear Scar, mm	0,71	0,71	0,7	0,66	0,65	0,7	0,7	0,67	0,60





As seen in table-9 weld load characteristic test results of TiO_2 NPs have better performance results at same ratios as compared to TiO_2 MPs in EB GO formulations.

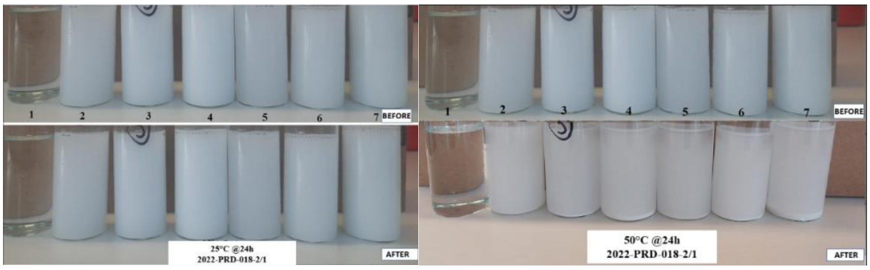
3.3 Stability Results of GO Formulation

Stability tests have been performed at both room temperature and 50ºC in oven.

Food Grade Gear Oil (FG GO)

Stability studies of FG GO formulations resulted that FG GOs are more stable at room temperature according to 50ºC stability conditions.

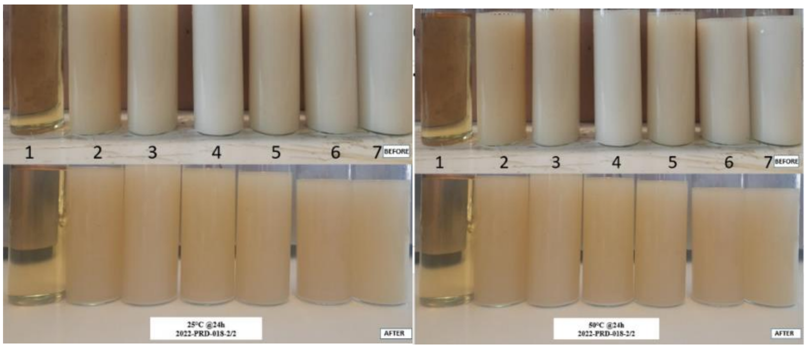
Figure-2: *Food Grade Gear Oil (FG GO) stability visuals*



Synthetic Gear Oil (Synthetic GO)

Stability studies of synthetic GO formulations resulted synthetic GO formulations are stable both at room temperature and at 50ºC.

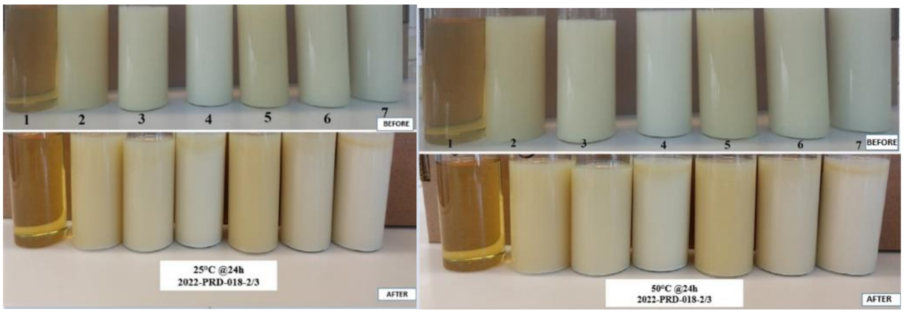
Figure-3: *Synthetic Gear Oil (Synthetic GO) stability visuals*



Traditional Gear Oil (Traditional GO)

Stability studies of traditional GO formulations resulted that traditional GOs are more stable at room temperature according to 50ºC stability conditions.

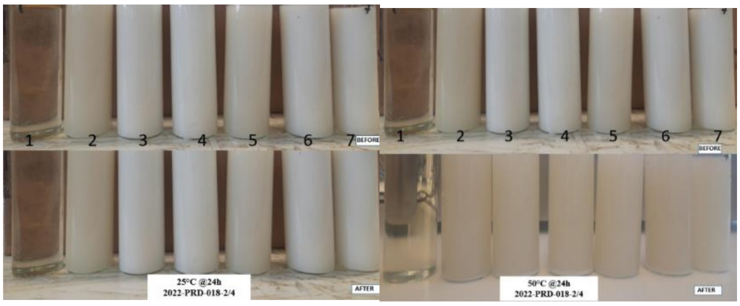
Figure-4: *Traditional Gear Oil (Traditional GO) stability visuals*



Ester Based Gear Oil (EB GO)

Stability studies of EB GO formulations resulted EB GO formulations are stable both at room temperature and at 50ºC.

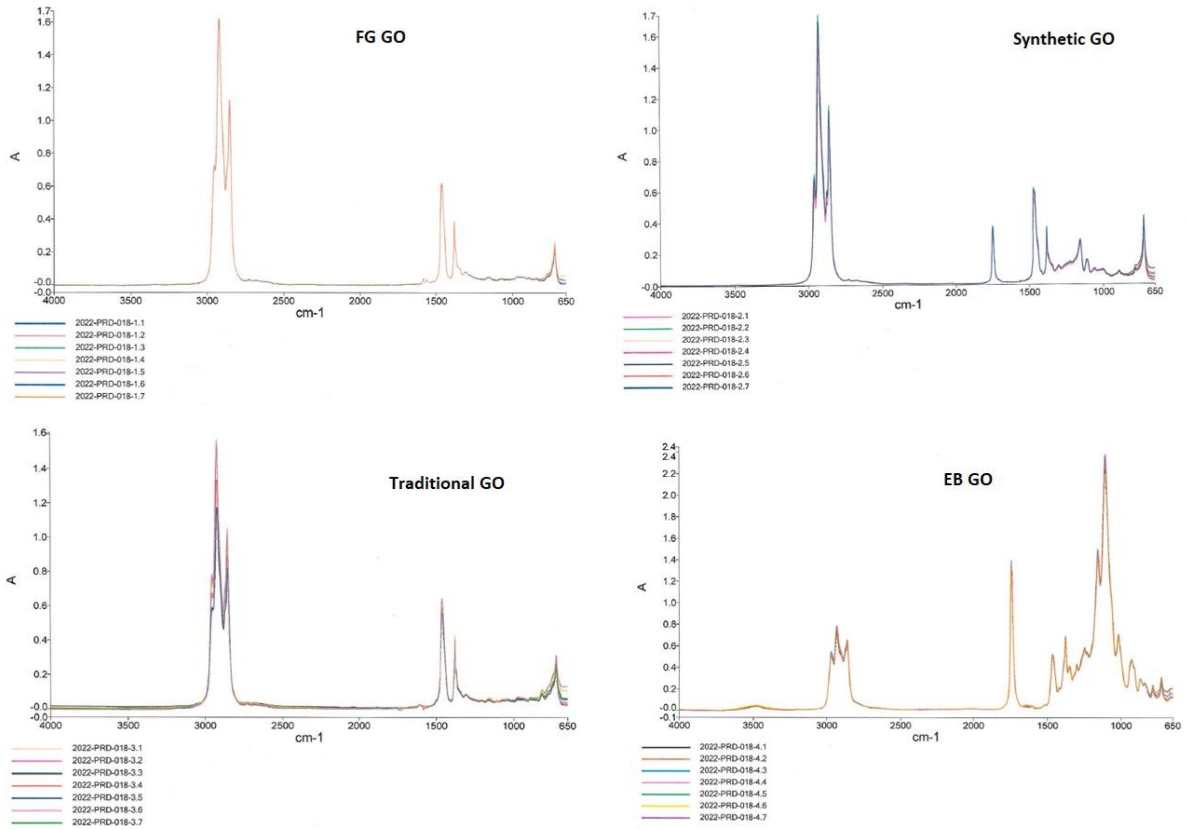
Figure-5: *Ester Based Gear Oil (EB GO) stability visuals*



3.4 FTIR Spectrums of GO Formulations

FTIR spectrum of GO formulations have not shown specific differences between different ratios of TiO_2 NPs and TiO_2 MPs at different base oil types.

Figure-6: *FTIR spectrums of GO formulations*



4. CONCLUSION

The conclusion section includes the answers to the main objectives of the study and the research questions, the findings obtained and the analysis of these findings. This section provides a summary of the data and analysis presented in the previous sections and highlights the main points of the study. Evaluation and interpretation of the findings in accordance with the research questions is the focus of this part of the study. In addition, an overview of the study, including its contributions, limitations, and possible future studies, is presented. The results section helps readers understand the key findings of the study and the overall implications of these findings. Acknowledgments to those who contributed to the study can be given in this section.

Sudeep I. et al[5] mentioned in their study that synthesis method of TiO_2 NPs and different type of modifications while synthesis effect the wear performance and friction coeffitiont of NP TiO_2. Ilie, Filip et al[8] mentioned on their study about the same phenomenon. They mentioned that different synthesis methods resulted different forms of TiO_2 NPs and different forms of TiO_2 NPs could show different tribological performances.

Sudeep I. et al[5] studied tribological behaviour of nano TiO_2 as oil additive and reported that nano formed TiO_2 could reduce and stabilize the coefficient of friction (COF) in base oil. They also reported that % 0,25 ratio TiO_2 resulted stable COF.

According to Gulzar et al.[16] lubrication mechanism of NPs are not known detaily yet. And one of the most important problems is stability of lubricants with NPs.

As conclusion:

1. Particle size differences of NPs and MPs has not a significant effect on food grade gear oil formulations. These results could be attributed to the test conditions. A. et al.[1] studied the effect of oil temperature and pressure on the contact surface on the performance of different gear oils and reported

that increasing in oil temperature and surface pressure resulted with increasing frictional performance and increasing tribo-film formation because of additive interactions despite that resulted with decreasing wear performance because of the near-surface hardening. And also, food grade white oils does not include any sulfur in their presence. Absence of sulfur could be one of the reasons of that low wear and weld performance results. Ilie, Filip et al[8] studied with TiO_2 NPs in an ecological friendly lubricant and they reported that COF reducing and lubricating potential of TiO_2 depend on the friction conditions.

A. et al.[1] reported that temperature of the oil film effects the friction decreasing with different types of gear oils. They also reported that friction reduction observed when temperature is between 80ºC-120ºC despite there was not friction decreasing observed at 30ºC working temperature.

2. NP and MP formulations showed better wear performances with TiO_2 from 0,2 % to 1 % ratios in FG GO formulations.

3. Particle size differences of NPs and MPs has not a significant effect on synthetic gear oil formulations likewise FG GO formulations.

W.R. Murphy et al.[4] studied with different types of base oils for gear oil formulations and reported that Poly Alpha Olefin type base oils and Poly Glycol type base oils reduces the surface contact temperature. We did not measure surface contact temperature in our study despite that very low wear scar results and higher weld load results according to FG GO formulations showed that synthetic GO formulations could forms better surface protection than FG GO formulations.

4. According to test results NP and MP formulations showed worse wear performances with TiO_2 from 0,2 % to 1 % ratios in synthetic GO formulations. Increasing on wear scar could be attributed to the test conditions likewise A. et al.[1]'s study.

5. Analysis results showed that especially in lower ratios TiO_2 NPs has better AW and EP characteristics according to TiO_2 MPs. Shubham Rajendra Suryawanshi et al.[13] studied and reported that wear scar diameter and COF values reduced with NP TiO_2 in commercial lubricants. This reduction could be sourced from the commercial lubricants have already AW and/or EP additives in them and NP TiO_2 could show synergistic performance together with AW and/or EP additives.

6. TiO_2 NPs showed better performance test results in EB GO formulations according to TiO_2 MPs. Krzan B. et al. [2] mentioned at their study that ester-based oils need generally less additive to perform the same performance characteristics according to mineral base oils. Despite that our test result shown on the contrary. Krzan B et all[2] studied different types of base oils for transmission fluids, and they reported that despite the good friction performances and lubricity characteristics of ester based fluids, they showed higher wear scars according to mineral oil based lubricants.

7. According to stability test results synthetic and EB GO formulations are more stable than traditional and FG GO formulations. For estimation of stability performances of final products, zeta potential measuring could be usefull tool.[16] According to stability test result there is no need that measurement because of low stability performances of final products. J.Qian et al[7] mentioned in their study stearic acid modified anatase microcrystal formed TiO_2 could made stabile dispersions in non polar solvents like lubricants. Shubham Rajendra Suryawanshi et al.[13] suggested that solubility of NP TiO_2 could be enchanced with using Oleic Acid. Further studies could work on it to increase the solubility and hot and room temperature stability of NP TiO_2 added gear oils. But addition of Oleic Acid could affect the corrosion performance and demulsibility performance of the Gear Oils. These two parameters must under control while usin Oleic Acid in Gear Oils. Chen, Y. et al.[15] investigated dispersion of NPs in lubricating oil and they concluded that to efficient dispersion of NPs in lubricating oils surface modification needs with a long alkyl chains. They also reported that parallel to Shubham Rajendra Suryawanshi et al.[13] for NPs with size smaller than 50 nm surfactan using a solution.

8. FTIR spectrum of GO formulations have not shown specific differences between different ratios of TiO_2 NPs and TiO_2 MPs at different base oil types.

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